

ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY

Periodic Technical Report

by

Prof. E. Peled

Sackler Faculty of Exact Sciences, School of Chemistry

Tel-Aviv University, Tel-Aviv, ISRAEL 69978

Second Periodic Report

(July 1989 - November 1989)

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

CONTRACT NUMBER DAJA45-89-C-0013

Ramot, Tel-Aviv University Authority for Research

and Industrial Development Ltd.

Approved for Public Release; distribution unlimited

DTIC
ELECTE
JAN 08 1990
S B D

The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the Contractor and the U.S. Government.

90 01 08 018

AD-A216 685

ADVANCED CALCIUM-THIONYL CHLORIDE HIGH-POWER BATTERY

Periodic Technical Report

by

Prof. E. Peled

Sackler Faculty of Exact Sciences, School of Chemistry

Tel-Aviv University, Tel-Aviv, ISRAEL 69978

Second Periodic Report

(July 1989 - November 1989)

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

CONTRACT NUMBER DAJA45-89-C-0013

Ramot, Tel-Aviv University Authority for Research

and Industrial Development Ltd.

Approved for Public Release; distribution unlimited

The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the Contractor and the U.S. Government.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release Distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			7a. NAME OF MONITORING ORGANIZATION		
6a. NAME OF PERFORMING ORGANIZATION Ramat-TA Univ. Auth. for App. Res. and Ind. Dev. Ltd.		6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code)		
6c. ADDRESS (City, State, and ZIP Code) 32 University Street, Ramat-Aviv, Tel-Aviv 61392, ISRAEL			9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAJA45-89-C-0013		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Army European Research Office		8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS		
8c. ADDRESS (City, State, and ZIP Code) 223/231 Old Marlebone Road London NW1 5TH ENGLAND			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) Advanced Calcium Thionyl Chloride High Power Battery					
12. PERSONAL AUTHOR(S) Prof. Emanuel Peled					
13a. TYPE OF REPORT 2nd Periodic Report		13b. TIME COVERED FROM 15/7/89 TO 15/11/89		14. DATE OF REPORT (Year, Month, Day) 89/ 11/15	
15. PAGE COUNT 22					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Calcium thionyl chloride battery, performance, shelf life, corrosion of calcium, characteristics of passive layers. High Energy density battery. SEI, calorimetry.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>In this phase we have demonstrated that an improved C-size Ca/TC A type cell can deliver at RT up to 5.5 Ah at low rates and 4.4 Ah at 0.9A rate. It has 10 to 80% more capacity than have commercial Li-TC and Li-SO₂ wound C-size cells. The improved Ca-TC cell lost almost no capacity after 4-5 weeks of storage at 70°C. It generates less heat at 20°C under OCV conditions than equivalent Li/TC cells, having the same electrode area, i.e. it has a longer shelf life. The improved shelf-life of calcium in BaX₂/TC solutions as compared to CaX₂/TC solutions results mainly from the difference in the solubility or reactivity of the CaO film in those two solutions. In CaX₂/TC solutions the oxide dissolves leaving the calcium with a CaCl₂ layer which does not provide the metal with good protection. In BaX₂/TC solutions, on the native CaO layer a BaCl₂·AlCl₃ or Al₂O₃ layer is formed. This BaCl₃·AlCl₃·Al₂O₃ layer does not form when the oxide is missing from the surface. Therefore cleaned calcium in BaX₂/TC solution corrodes at the same rate as does calcium in CaX₂/TC solutions.</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL R. R. F.			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

CHAPTER 1: A 5.5 Ah Ca/Sr(AlCl₄)₂-SOCl₂ C-Size Cell

The calcium-thionyl chloride (TC) cell is considered as a safer alternative to high-power lithium cells.⁽¹⁻³⁾ There is a high probability that it can be developed⁽⁴⁾ as a safe, vent-free cell which will not rupture or leak over a wide range of abusive conditions. The major drawback of the Ca-TC cell has been rapid corrosion of the calcium anode (i.e. too short a shelf life). This high rate of corrosion in the CaX₂ (X=AlCl₄) electrolyte results from the fact that the CaCl₂ SEI does not provide the calcium anode with sufficient corrosion protection^(4,5). This problem has been successfully solved by replacement of the CaX₂ electrolyte by SrX₂ or BaX₂ electrolytes^(5,6). These substitutions improved both the morphology and chemical composition of the passivating layer which covers the calcium anode. The addition of SO₂ to the electrolytes affects the morphology of the passivating layer and further decreases the corrosion rate of calcium^(6,7). A calorimetric study⁽⁸⁾ of the Ca/SrX₂-SOCl₂ cell revealed that the Faradaic efficiency of the calcium anode is about 0.9 at 30°C, and that there is no loss of capacity after four weeks' storage at 70°C.

The goal of this work was to demonstrate that the Ca/SrX₂-TC cell can be developed, not only as a safe cell, but also as a premium long-life high-power cell with very high energy density.

Previous work^(4,8) has indicated that a) the Ca-TC cell generates excessive heat at high discharge rate especially at elevated temperatures, b) that the Faradaic efficiency decreases with current density and temperature. Thus we decided to increase the active electrode area from 150 cm² (4,5,7) to 200-220 cm² and in this way to reduce the current density. The effect of this change can be seen in Fig.1 and Table 1. Information on cell components and assembly can be found in Refs. 4,7 and 8. The "old" Ca/TC cell



Dist

Special

A-1

for
<input checked="" type="checkbox"/>
<input type="checkbox"/>
<input type="checkbox"/>
on
on
ty Codes
and/or
Special

in Fig.1 had 150 cm^2 electrode area and a 50μ thick Tefzel separator of 60% porosity (Scimat) while the "improved" Ca/TC cell had 200-220 cm^2 electrode area and a Tefzel separator of 80% porosity. Both cells had the same electrolyte - $0.84\text{M Sr}(\text{AlCl}_4)_2 + 7\%(\text{v/v})\text{SO}_2$ (or $20\% \text{SO}_2$). The cells were discharged either at 30 or 55°C inside a home-made calorimeter (7,8), or at RT. The improved Ca/TC cell has about 30% more capacity than the "old" Ca/TC cell. At low discharge rates the improved Ca/TC cell has 10% and 80% more capacity than a wound SAFT Li/TC C-size cell and a wound Duracell C-size Li/ SO_2 cell respectively. At 0.9A rate it has 50% more capacity than either of these cells.

The increase of SO_2 concentration from 7 to 20% (v/v) does not seem to have a major effect on the cell capacity at RT discharge, on the heat flux during discharge, or on the Faradaic efficiency. However, it significantly decreased the heat output (under OCV conditions), i.e. the self-discharge rate (Fig.2). It can be seen that, when adjusted to the difference in electrode area, the heat output of the "old" Ca/TC cell with 7% (v/v) SO_2 is similar or smaller than that of Li-TC cells. However, the improved Ca/TC cell with 20% SO_2 generates much less heat than do either the Li/TC (bobbin or wound) cell or the Ca/TC cell with 7% SO_2 . This is in good agreement with the results of calcium corrosion tests⁽⁷⁾. Ca/TC cells with either 7 or 20% SO_2 performed very well in a 4-5 week 70° storage tests with minor loss in capacity (Table 1). Moreover, cells that were stored for 5 weeks at 70°C and an additional 10 months at RT (Fig.3) lost less than 2% capacity. This storage affects neither the Faradaic efficiency nor the heat generation rate during discharge. It caused a 0-70 mV voltage penalty at high discharge rates (Table 1).

To conclude, the improved Ca/ $\text{SrX}_2\text{-SOCl}_2\text{+SO}_2$ cell has, at RT discharge, 10-80% more capacity than do commercial Li/TC and Li/ SO_2 cells, it loses

almost no capacity after 4-5 weeks of storage at 70°C, and it generates less heat at 20°C under OCV conditions than equivalent Li/TC cells having the same electrode area, i.e. it has a longer shelf life.

References

1. E. Peled, Proceedings of the 32nd Power Sources Symposium, p. 445 (1986).
2. C. Walker, Jr., W. Wade, M. Binder and S. Gilman, J. Electrochem. Soc. 133, 1555 (1986).
3. Staniewicz, Proceedings of the 33rd Power Sources Symposium, p.144. The Electrochem. Soc. 1988.
4. E. Peled, ibid p.136.
5. E. Elster, R. Cohen, M. Brand, Y. Lavi and E. Peled, J. Electrochem. Soc. 135, 1307-1308 (1988).
6. E. Peled, E. Elster, J. Kimel and M. Brand US Pat No. 4,755,440.
7. E. Peled, First Periodic Report to the US Army, No. DAJA45-89-C-0013, July 1989.
8. R. Cohen, Y. Lavi and E. Peled, J. Electrochem. Soc., submitted.
9. M. Pallivathikal, H. Yamin and U. Zak, J. Electrochem. Soc. 176th Meeting, Florida Oct. 1989.
10. R. Lutwack Personal communication.

TABLE 1:

The Effect of SO₂ Concentration, RT and 70°C Storage and Electrode area on performance.

Code Cell El. area (cm ²)	[SO ₂] [%]	Storage Condition	load (Ω)	Average Voltage (V)	Discharge Temp. (°C)	Capacity (to 2V) (Ah)	W _T (W)	ε	
Q ₁₂ (150)	7	Fresh	4	2.56	55	3.7	1.2	84	ref.8
Q ₆ (150)	7	1	4	2.56	55	3.6	1.21	83	ref.8
Q ₁ (150)	7	2	6.6	2.55	55	3.8	0.59	85	
Q ₁₁ (150)	7	Fresh	9.4	2.39	30	3.4	0.49	88	ref.8
Q ₂₀ (150)	7	1	9.4	2.39	30	3.4	0.46	89	ref.8
Q ₁₈ (150)	7	2	9.4	2.35	30	3.34	0.46	88	
Q ₁₀ (150)	7	Fresh	4	2.30	30	2.2	1.1	88	ref.8
Q ₂ (150)	7	1	4	2.30	30	2.2	1.1	89	ref.8
S ₁₈ (200)	7	Fresh	4	2.40	30	3.7	1.1	89	
S ₂₀ (200)	7	4	4	2.33	30	4.0	1.1	89	
T ₁₃ (220)	20	Fresh	4.05	2.45	55	4.2	1.2	84	
T ₁₀ (220)	20	Fresh	3	2.45	RT	4.4			
T ₁₈ (220)	20	4	2.9	2.40	RT	4.05			
S ₁₇ (200)	7	Fresh	3	2.55	RT	4.4			
T ₄ (220)	7	Fresh	2.6	2.55	RT	4.2			
S ₁₉ (200)	7	3	113	2.76	RT	5.48			
T ₇ (220)	20	5	19.5	2.50	RT	5.0			
T ₁₇ (220)	7	5	42.5	2.61	RT	5.23			

- | | |
|--------------------------------------|--------------------|
| 1. 5 weeks at 70°C + 4 weeks at RT | 4. 4 weeks at 70°C |
| 2. 5 weeks at 70°C + 10 months at RT | 5. 3 months at RT |
| 3. 6 months at RT | |

Figure Captions

Fig.1. Plots of room temperature capacity vs current for different C-size cells: *-Improved $\text{Ca/SrX}_2\text{-SOCl}_2\text{+SO}_2$ cell; O-SAFT LSH14; Δ - $\text{Ca/SrX}_2\text{-SOCl}_2\text{+SO}_2$ "old" cell; -Duracell LO28SH cell.

Fig.2. Comparison of 20°C heat output under OCV conditions of C-size or equivalent size lithium and calcium TC cells: 1-Li-TC, AA/2 size bobbin type 5 cm² electrode area, values were multiplied by 44 (from ref.9); 2-Li-TC, AA size bobbin type 14 cm² electrode area, values were multiplied by 15.7 (from ref.9); 3-Li-TC D-size wound cell, values were divided by 2 (from ref.10); 4- $\text{Ca/SrX}_2\text{-SOCl}_2 + 7\% \text{SO}_2$ 150 cm²; 5- $\text{Ca/SrX}_2\text{-SOCl}_2 + 20\% \text{SO}_2$, 220 cm².

Fig.3. Heat output measured at 20°C under OCV conditions of C-size $\text{Ca/Sr}^{++}\text{+}7\% \text{SO}_2$ cells which have been stored for 5 weeks at 70°C.

FIG.1 COMPARISON BETWEEN C-SIZE CELLS

RT Discharge

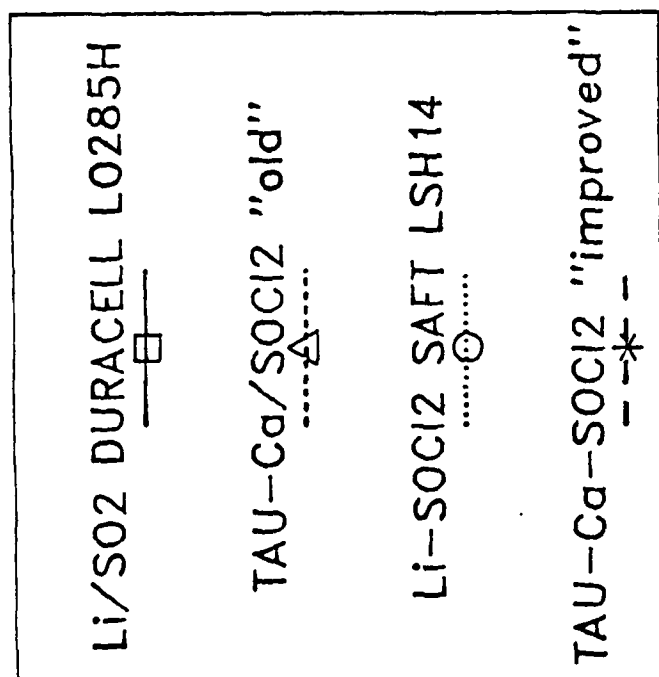
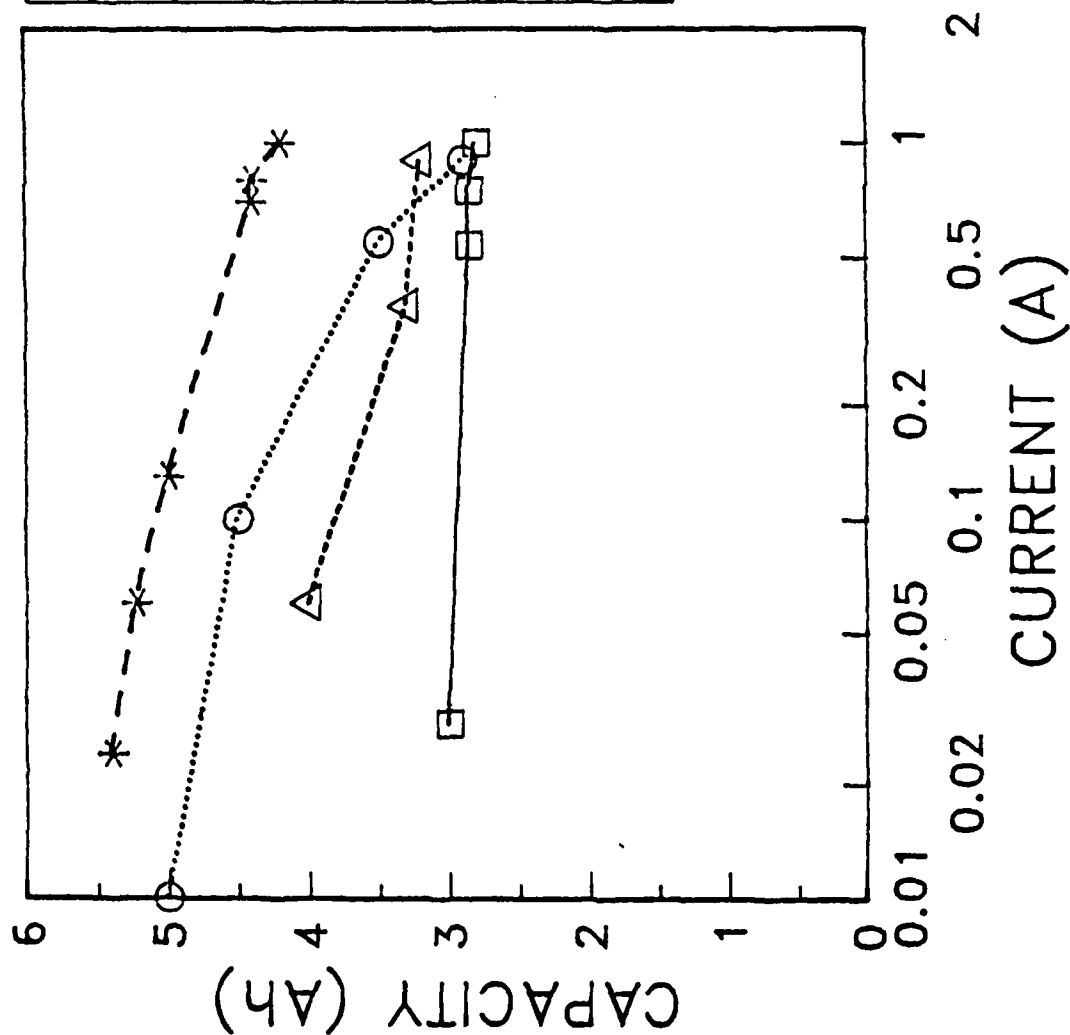


FIG. 2 Heat Output of Wound Cells
C-size or Equivalent

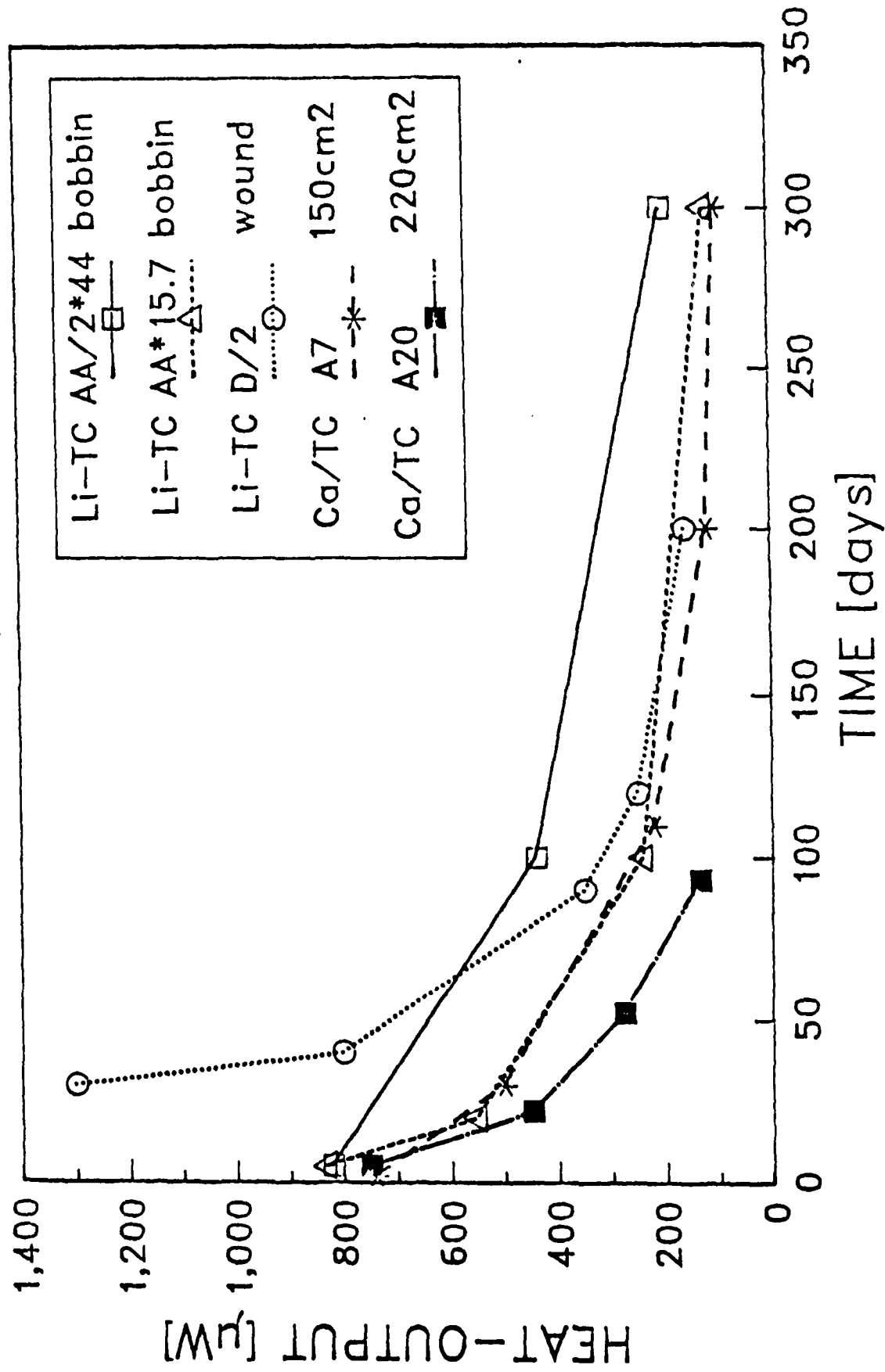
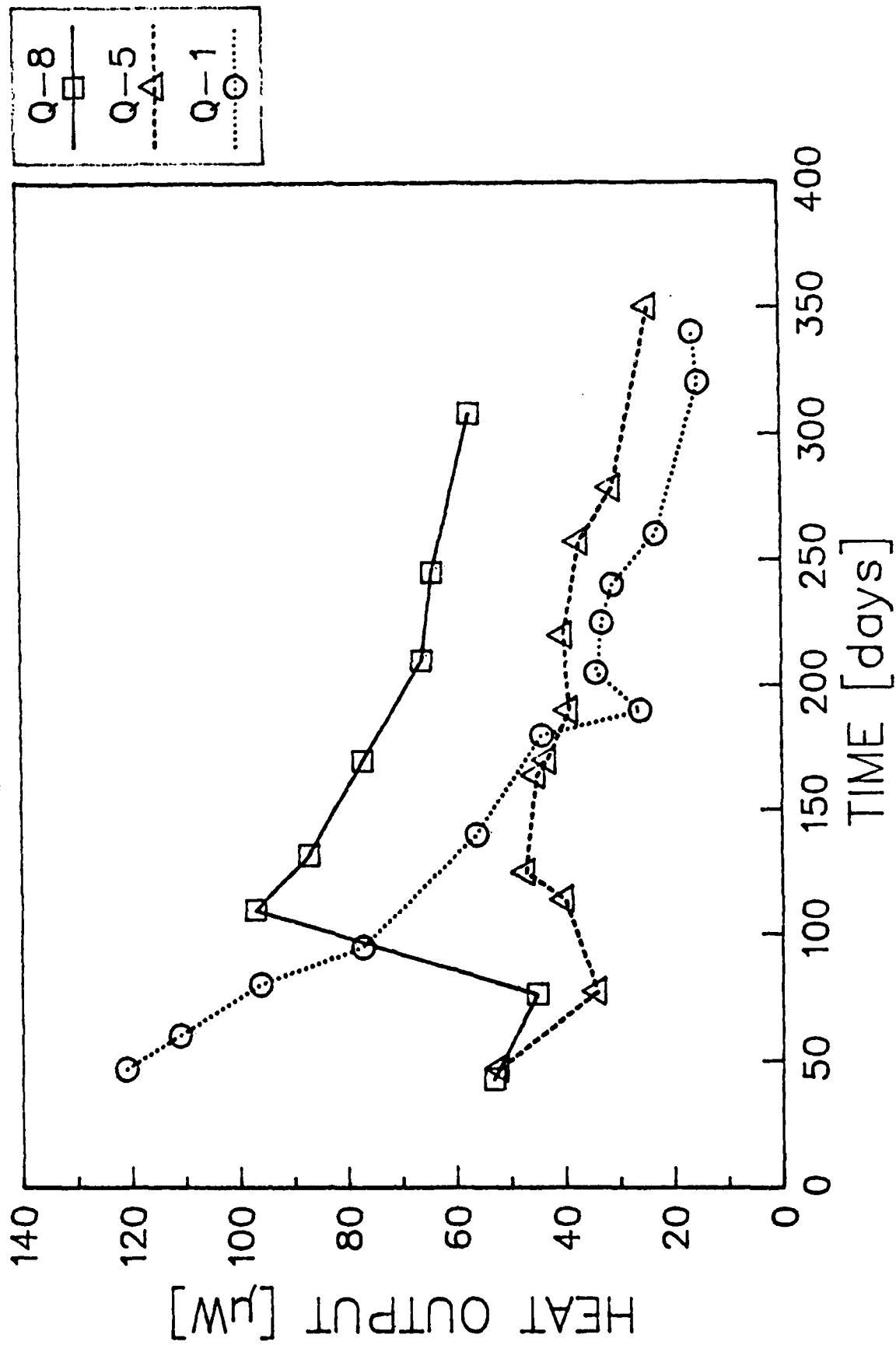


Fig.3 Heat Output of Ca-TC A7 C-size cells
after storage of 28 days at 71C



2.1 INTRODUCTION

Efforts were being made in our laboratory to increase the shelf-life of calcium-thionyl chloride batteries, i.e. to decrease the corrosion rate of calcium in thionyl chloride solutions. The result of these efforts has been the development of two different systems. In one, the CaX_2 ($\text{X}=\text{AlCl}_4$) salt dissolved in the thionyl chloride was replaced with SrX_2 and in the other it was replaced by BaX_2 [1].

Calcium in the Ca/TC system is an SEI [2] electrode, and the solid electrolyte which covers the calcium metal governs the rate of the reaction between the metal and the thionyl chloride solution- the corrosion rate. Therefore changes in the corrosion rate following replacement of the electrolyte salt are connected to changes in the film.

As a result of previous studies it became clear that the native oxide film covering the calcium metal foil plays a greater and more complex role in determining the corrosion and performance characteristics of the calcium electrodes Than has been believed up to now.

The goal of this work was to study the effect of surface treatment on the behavior of the film found in these thionyl chloride solutions.

Samples of calcium foil whose surface has been treated in various ways were examined:

Untreated calcium: calcium used as received,

Sandpapered calcium: calcium was abraded inside the glove box

with number 1 sandpaper,

Chemically cleaned calcium: calcium was immersed in 1% HCl in ethanol until its surface was shiny and immediately transferred into pure thionyl chloride in order to form CaCl_2 film. All these operations were carried out in the glove-box. Calcium metal used throughout this work was purchased from Pfizer and is from two batches: 1) batch 1983 (A)- 99.5% purity calcium strips, rolled in a non-controlled atmosphere room and shipped in mineral oil, 2) batch 1986 (B)- 99.5% calcium strips rolled in a glove box and shipped under argon.

This report summarizes the results obtained so far in the BaX_2/TC system .

2.2 CORROSION RESULTS

Corrosion of calcium strips in BaX_2/TC solutions was studied at elevated temperatures (71°C) and at RT. At 71°C this was done by measuring the amount of calcium remaining in the ampules, or the capacity remaining in C-size cells after storage. At RT the corrosion rate was measured during the storage period by a microcalorimeter with a 20.00°C bath temperature, and by measuring the remaining capacity in C-size cells at the end of the storage period.

2.2.1 Corrosion of calcium stored in ampules at 71°C.

Strips of untreated calcium and abraded calcium were prepared from batch A, and strips of untreated and chemically cleaned calcium were prepared from calcium batch B. The amount of calcium remaining after the storage period was determined by immersing the

calcium in water and titrating the resulting Ca(OH)_2 with HCl . The results are summarized in table 2-1. Calcium samples were stored simultaneously in CaX_2/TC for reference. The results of calcium stored in CaX_2 are also given in table 2-1. In each batch, samples of calcium which were not stored at all were titrated with HCl in order to determine the amount of CaO in the sample. Corrosion results shown in table 2-1 are corrected for the amount of oxide, that is they are based on the loss of calcium metal only.

2.2.1.1 CaX_2 solutions.

Examination of the results of storage in CaX_2 shows very high corrosion ($\approx 20 \mu\text{A}/\text{cm}^2$) for chemically cleaned calcium (batch B) i.e. calcium that was almost completely deprived of its native protective layer, which is probably oxide, and for abraded calcium (batch A), in spite of the film that seems to cover abraded calcium after annealing. Although the corrosion rate is similar for both these categories, the corrosion mechanism seems different. Abraded calcium samples of batch A were pitted over their whole surface. Cleaned calcium samples of batch B were slightly pitted on the periphery only, indicating homogeneous corrosion of the sample area.

Untreated calcium of batches A and B showed less corrosion than treated calcium. Batch B which had a thicker oxide layer (13 mg CaO in 100 mg sample in batch B compared to 5.3 mg CaO in 100 mg sample in batch A) had less corrosion.

2.2.1.2 BaX_2 solutions

Examination of the results of storage in BaX_2 solutions shows that samples of abraded calcium of batch A exhibit the lowest corrosion current in this set of experiments, with no significant

difference between untreated calcium covered by its native oxide film or abraded calcium covered with a thin oxide film. On the basis of four weeks at 71°C being equivalent to three years at RT, the result of $7\mu\text{A}/\text{cm}^2$ at 71°C is equivalent to $0.2\mu\text{A}/\text{cm}^2$ at RT.

Chemically cleaned calcium showed the highest corrosion rate. It is interesting to note that for cleaned calcium the corrosion rate is similar in CaX_2 and BaX_2/TC solutions.

2.3 SEM TESTS-MORPHOLOGY AND COMPOSITION OF THE FILM

Samples of treated and untreated calcium of batch B were stored in 0.75M BaX_2 for periods ranging from 1 hour to 10 months at RT and 28 days at 71°C. The morphology of the surface, and of cross sections was studied with the use of SEM equipped with an X-ray analyzer.

2.3.1 Chemically Cleaned Calcium.

The results are summarized in table 2-2. The atomic percentage of the elements is calculated on the assumption that the sum of the analyzable elements is 100%. The column "%total" in the table states the percent reflection of the surface relative to the reflection expected for the composition measured. A low %total may be due to an undetectable element (for the X-ray) on the surface or a surface which is not smooth.

Room temperature tests :In samples stored at RT two regions could be observed. One was shiny, with the surface appearing as immediately after cleaning. The other seemed to be covered

with some layer. It was found that the samples were covered on both sides with a very thin chloride layer. This was concluded from high %total and excess calcium. Thus metallic calcium was measured together with the CaCl_2 layer. It is hard to tell how much of the small amount of chlorine is combined with Ba as BaCl_2 , and how much as CaCl_2 . If we assume that all the barium on the surface exists in the form of BaCl_2 , it seems that some regions remain as CaCl_2 with no barium at all, and some are enriched with barium. In areas that were richer in barium than the starting concentration of 0.1-0.2 atomic percent, there was also sulfur.

71°C tests In one month-71°C storage tests, two very distinct areas were found. A dark grey region and a higher white area surrounding it. The two areas are chloride areas. The grey one- a CaCl_2 layer, and the white one- a $\text{BaCl}_2/\text{CaCl}_2$ layer with more BaCl_2 than CaCl_2 . ($\text{Ba}:\text{Ca}=1.27$).

If we adopt the findings at RT that some areas become progressively enriched with barium and some are not, the results at 71°C show the same behavior. The reason may be that there are distinct anodic and cathodic areas. In the anodic areas calcium is dissolved, precipitating as CaCl_2 following migration of Cl^- through the CaCl_2 film. In the cathodic areas thionyl chloride is reduced, thus leaving some sulfur on the area. In these areas the concentration of BaCl_2 rises and BaCl_2 precipitates. After one month at 71°C there is much barium in this region, but almost no sulfur. It may be that sulfur is soluble at 71°C.

Aluminum was found at low concentrations (up to 3%) only in samples with low %total, i.e. surfaces that were not thoroughly

cleaned. In chemically cleaned samples there is no Al compound on the surface.

2.3.2 Untreated Calcium.

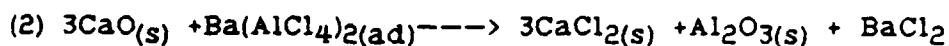
The results of the elemental analysis of untreated calcium (batch B) samples stored in BaX_2/TC solution at RT and at 71°C are summarized in table 2-3.

RT tests: The appearance of the samples is that of a plain surface with lumps of crystals on it. The amount of the crystals on the surface increases with the duration of storage in the solution until after 10 months of storage the whole surface is covered, and the analysis of a crystal and of average surface is similar.

The elemental analysis shows that the surface is covered with a thin BaCl_2 layer together with an aluminum chloride and/or oxide. Because this layer is thin it is analyzed together with calcium metal beneath it. Crystals are thicker than the layer and therefore less calcium from underneath the layer appears. The %total increases with time indicating a slow decrease in the oxygen content of the layer. The percentages of Cl and Ba increase, while Ca percentage decreases. At the beginning of storage the amount of Cl fits $\text{BaCl}_2 + \text{AlCl}_3$. After a few days (2 days for crystals and 1 week for plain surface) the amount of Cl does not correspond to all the Al being in the form of AlCl_3 and it seems that some of the Al exists in a compound with an undetectable element, probably oxygen.

The CaO native film may react with the electrolyte

in two parallel ways; with thionyl chloride (1), and with adsorbed BaX_2 (2). Both reactions are thermodynamically feasible.



(Estimation of the the free energy change for reaction (2) was made using reaction (3))



It seems that two processes occur on the surface of calcium samples covered with CaO:

I) Reaction between CaO and thionyl chloride.

II) Reaction between the CaO and BaX_2 adsorbed on the surface.

This process occurs in two stages:

a) $\text{Ba}(\text{AlCl}_4)_2$ ($\text{BaCl}_2 \cdot \text{AlCl}_3$) precipitates on the surface.

b) Some of the AlCl_4^- reacts with the CaO and Ba^{++} to give $\text{CaCl}_{2(s)}$, $\text{Al}_2\text{O}_{3(s)}$ and $\text{BaCl}_{2(s)}$.

This reaction is very slow, as evidenced by a sample stored for 10 months at RT. On the surface the sample contained BaCl_2 (18%), CaCl_2 (5.6%), some AlCl_3 and a little Al_2O_3 with a very high total (85-91%). In a cross section it was revealed that under that layer existed a layer with a very low total (43-44%) with no Ba or Al, probably a CaO layer.

By processes a) and b) the surface is depleted of CaO but enriched with BaCl_2 , CaCl_2 , AlCl_3 and Al_2O_3 .

Barium content increases with time up to a maximum of 18 atomic percent after 10 months of storage at RT. Aluminum content on the surface reaches a maximum after one week of storage.

71°C tests:

At 71°C Al content decreases with time of storage in all the areas and the %total increases. Areas rich in CaCl_2 do not contain Al (0.95% after 10 days of storage, 0.37% after 28 days of storage) and areas rich in Ba contain some Al, which decreases with time of storage at 71°C to 3% after 28 days. It seems that the oxide layer dissolves with time, and with it the Al-compound-containing layer. As $\text{CaO} + \text{Al}$ decrease with time, the surface is left with a quit pure CaCl_2 layer which does not provide good corrosion protection to the calcium. Corrosion sets in as for cleaned calcium and two distict areas can be seen. One area becomes depleted of BaCl_2 with time (12% Ba after 10 days, 1-4% after 24 days and 0.5% after 28 days). The second area becomes enriched with BaCl_2 .

2.3.3 Summary of SEM-X-ray Results

In the elemental analysis the difference between samples that were cleaned and untreated samples is seen again. In chemically cleaned calcium, which was deprived of its oxide layer and given a CaCl_2 layer, the outer layer is CaCl_2 with some barium in part of the areas. The only observations of distinct amounts of barium and aluminum were found in the case of inadequately cleaned samples. In the cleaned samples there probably exist two areas: one which is enriched in barium and is the cathodic area and the other a pure CaCl_2 , the anodic area.

In untreated calcium, covered with an oxide layer, the CaO is quit stable. On top of it BaCl_2 and some compound of Al with Cl and probably O precipitate, forming round lumps of crystals. This process is homogeneous on the surface. Upon storage at 71°C, the

CaO reacts with the electrolyte, the situation becomes similar to that for chemically cleaned samples, and two areas are formed. The cathodic BaCl_2 area and the anodic CaCl_2 area.

2.4 AC RESULTS

AC measurements were made on untreated, abraded and chemically cleaned calcium electrodes with the use of hermetically sealed three-electrode cells in 0.75M BaX_2 solution.

The results show:

SEI Resistivity- Resistivity at $20 \pm 5^\circ\text{C}$ after 10-100 days of storage ranges between 40×10^{10} - $200 \times 10^{10} \Omega \cdot \text{cm}$. Abraded electrodes have the highest resistivity, untreated have lower resistivity and cleaned electrodes the lowest.

SEI Thickness- Two electrodes that were stored in a glove-box for more than a month between cell assembly and filling showed a relatively thick SEI of about 200-500Å. All other electrodes had SEI thickness ranging between 20 to 75Å from the first day of filling. From the ac results the importance of the oxide covering the calcium is obvious. In the case of cleaned calcium there is a rise in the resistivity during the first 20 days of storage. Afterwards the resistivity remains constant but a decrease in the thickness occurs, resulting in a decrease in the resistance. Untreated and abraded electrodes show a common behavior. An SEI is formed with a constant thickness and increasing resistivity. The resistivity of these electrodes is much higher than that of the cleaned calcium.

In corrosion tests, as well, the results for untreated and abraded calcium were similar, while corrosion of cleaned calcium was much

higher. This parallel behavior suggests a connection between high ionic resistivity and low corrosion. Corrosion depends upon the electronic resistivity (R_e), and the connection between R_i (ionic resistivity) and corrosion suggests that in these cases the building of a layer with higher R_i and higher R_e occurs.

2.5 SUMMARY

The improved shelf-life of calcium in BaX_2/TC solutions as compared to CaX_2/TC solutions results mainly from the difference in the solubility or reactivity of the CaO film in those two solutions. In CaX_2/TC solutions the oxide dissolves leaving the calcium with a $CaCl_2$ layer which does not provide the metal with good protection. In BaX_2/TC solutions, on the native CaO layer a $BaCl_2+AlCl_3$ or Al_2O_3 layer is formed. This improves the corrosion resistance of the passive layer. This $BaCl_3+AlCl_3+Al_2O_3$ layer does not form when the oxide is missing from the surface. Therefore cleaned calcium in BaX_2/TC solution corrodes at the same rate as does calcium in CaX_2/TC solutions.

References

- 1) UK patent Application GB 2187590A.
- 2) E. Peled, J. Electroch. Soc. 126, 2047 (1979).

Table 2-1: Summary of corrosion results for calcium stored in CaX_2/TC and BaX_2/TC solutions in ampules at 71°C.

Calcium Batch treatment	electrolyte	storage time (days)	weight loss of metal (%)	corrosion current ($\mu\text{A}/\text{cm}^2$)
A, untreated	CaX_2 1M	24	18±3	14±2
B, untreated	CaX_2 0.75M	28	17±2	11±1
A, abraded	CaX_2 1M	24	22±5	21±5
B, chem. clea.	CaX_2 0.75M	28	24±3	20±3
A, untreated	BaX_2 1M	24	10±3	8±2
A, abraded	BaX_2 1M	24	8±2	7±2
B, chem. clea.	BaX_2 0.75M	28	24±1	21±1

A: batch 1983, published before in [1], B: batch 1986

Elemental analysis for chemically cleaned Ca in Ba(AlCl₄)₂/TC solutions

period	1hour mat	1hour shiny	1 day dark	1 day shiny	2 days	1 week	1month	1month 71C grey	white
Al	0.15	0.08	0.38	0.03	0.05	0.00	3.0	0.07	6.40
Cl	7.76	1.34	14.30	1.15	9.00	2.80	29.6	59.80	65.0
Ca	91.40	98.50	84.40	98.60	30.00	97.00	69.5	39.70	15.0
Ba	0.34	0.04	0.39	0.14	0.20	0.07	5.3	0.25	19.0
S	0.30	0.03	0.39	0.00	0.40	0.07	1.9	0.04	0.13
Total	87.00	90.00	72.00	90.00	78.00	88.00	73.0	87.00	87.0

Table 2-2:Elemental analysis results for chemically cleaned calcium stored in BaX₂/TC solution at RT and 71°C.

Untreated Calcium in BaX2 Solutions

Table 2-3: Elemental analysis results for untreated calcium stored in BaX₂/TC solution at RT and 71°C.

	1hour	24hours	48hours	48h	1week	1week	1month	10months	10d71	1month71					
		crystal	surface	crystal	surface	crystal	crystal	surface	grey	white	crystal				
											surface				
Al	1.90	5.70	1.70	3.8	1.10	16.40	4.40	7.1	14.60	9.7	7.4	0.95	6.5	2.97	0.37
Cl	8.40	17.90	7.50	18.0	6.20	48.70	14.00	33.0	43.00	61.6	61.4	52.00	60.6	58.80	64.70
Ca	87.00	71.20	89.00	71.5	91.20	20.70	77.60	8.2	4.29	5.8	8.4	24.00	5.5	5.30	34.20
Ba	1.50	4.10	1.10	5.0	1.00	10.80	2.89	5.3	8.70	18.2	18.1	12.00	26.5	32.50	0.47
S	0.44	0.72	0.54	1.0	0.33	2.73	0.73	2.4	4.50					0.20	0.00
Total	10.00	66.00	69.00	71.0	70.00	76.00	72.00	34.0	71.00	91.0	85.0	86.00	86.0	88.00	89.00